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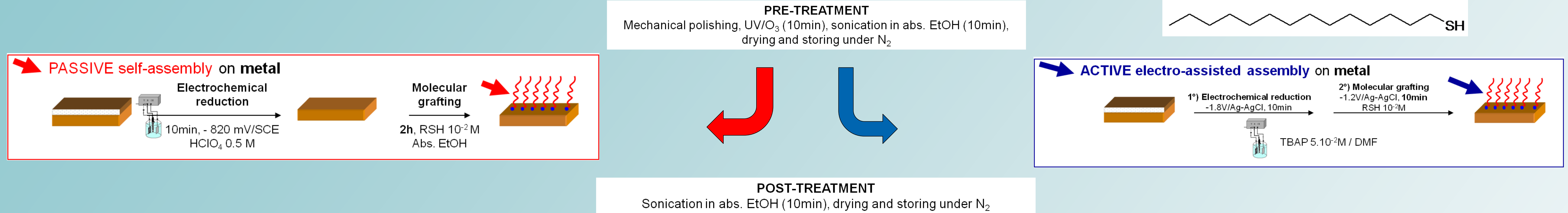
Electro-assisted formation of organothiols self-assembled monolayers on polycrystalline copper surfaces

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General context: organothiols films grafted on copper

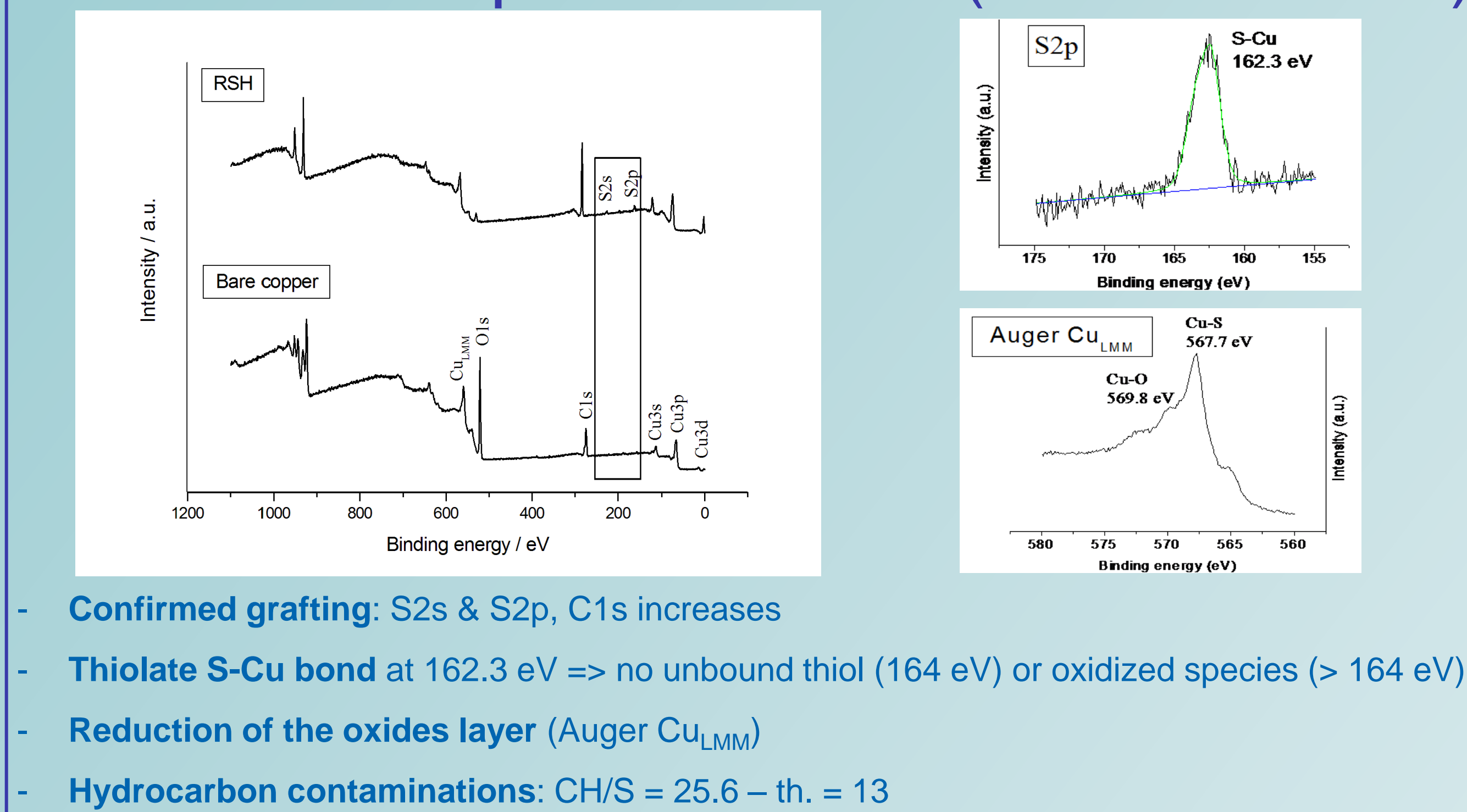
- Organothiol Self-Assembled Monolayers (SAMs)** can be successfully adsorbed on noble (Au) and **oxidizable metals** (Cu, Zn, Ni). They can be used as protective coatings against corrosion, lubricants, lithographic patterns, molecular (bio)sensors, ... [1]
- Oxidation state of the substrate surface** is a key factor for the SAMs formation => an **electrochemical reduction pretreatment of the Cu oxides layer** can be exploited to form **reproducible high quality films** [2].
- Molecular adsorption process** has an important impact on the SAMs characteristics: **passive self-assembly** (open circuit potential) **vs. active electro-assisted assembly** (cathodic polarization of Cu) [3].

Two experimental approaches and methodologies



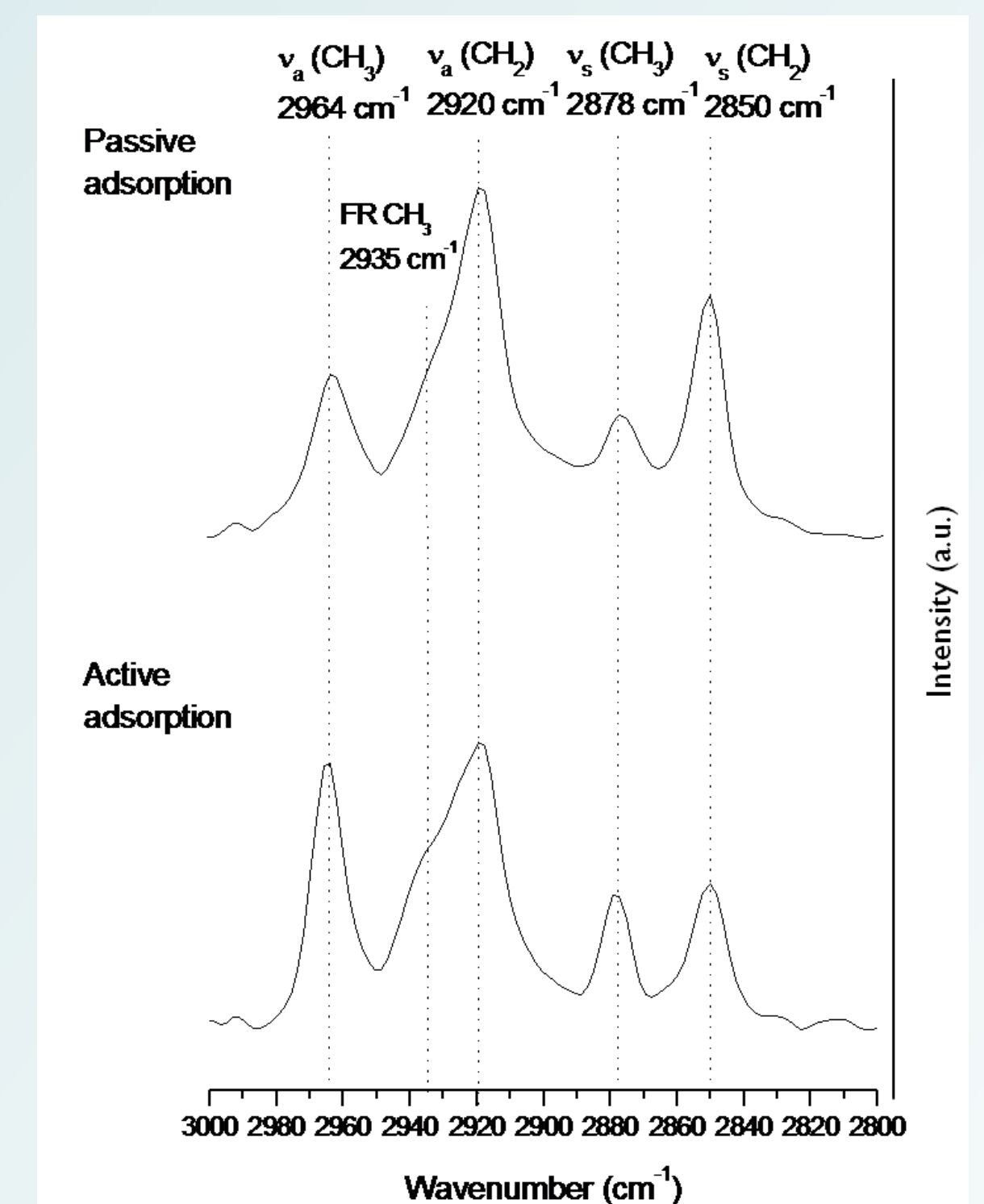
Results and discussion

Chemical composition: XPS (active method)

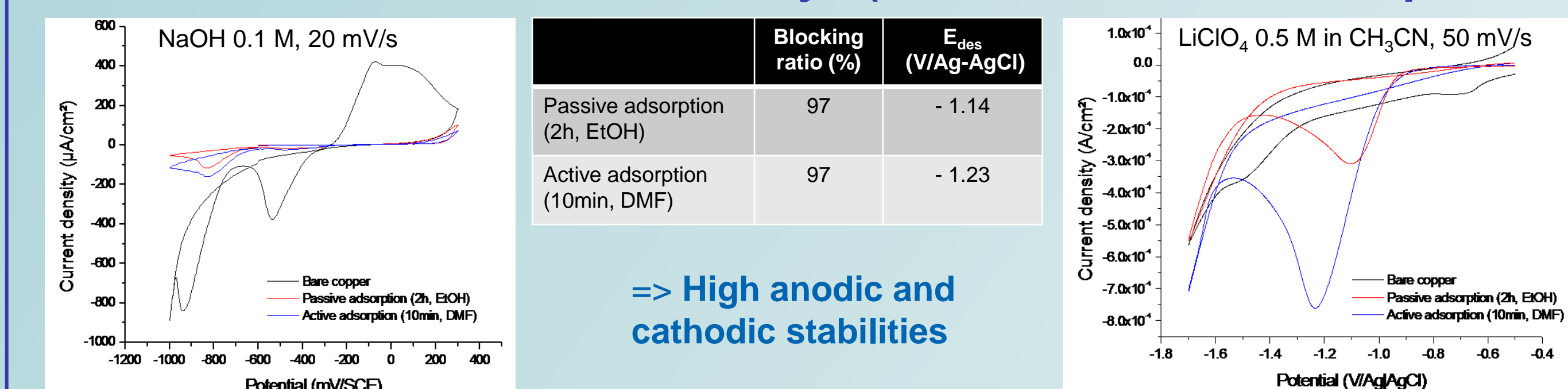


Structure and organization: PM-IRRAS

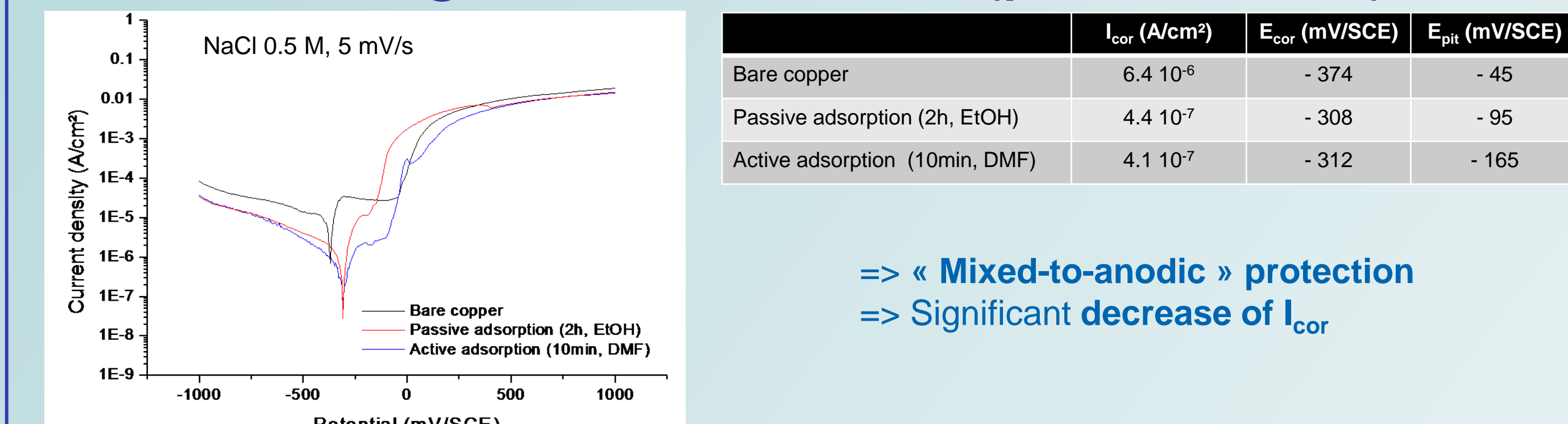
- $\nu_a(\text{CH}_2) = 2920 \text{ cm}^{-1}$ and $\nu_s(\text{CH}_2) = 2850 \text{ cm}^{-1}$ => in both cases, **densely packed monolayers** with alkyl chains in a **trans zig zag conformation**
- Intensity of CH₃ bands more important with the active adsorption process** => **modification of the alkyl chain inclination and orientation relative to the substrate surface** due to the cathodic polarization of Cu



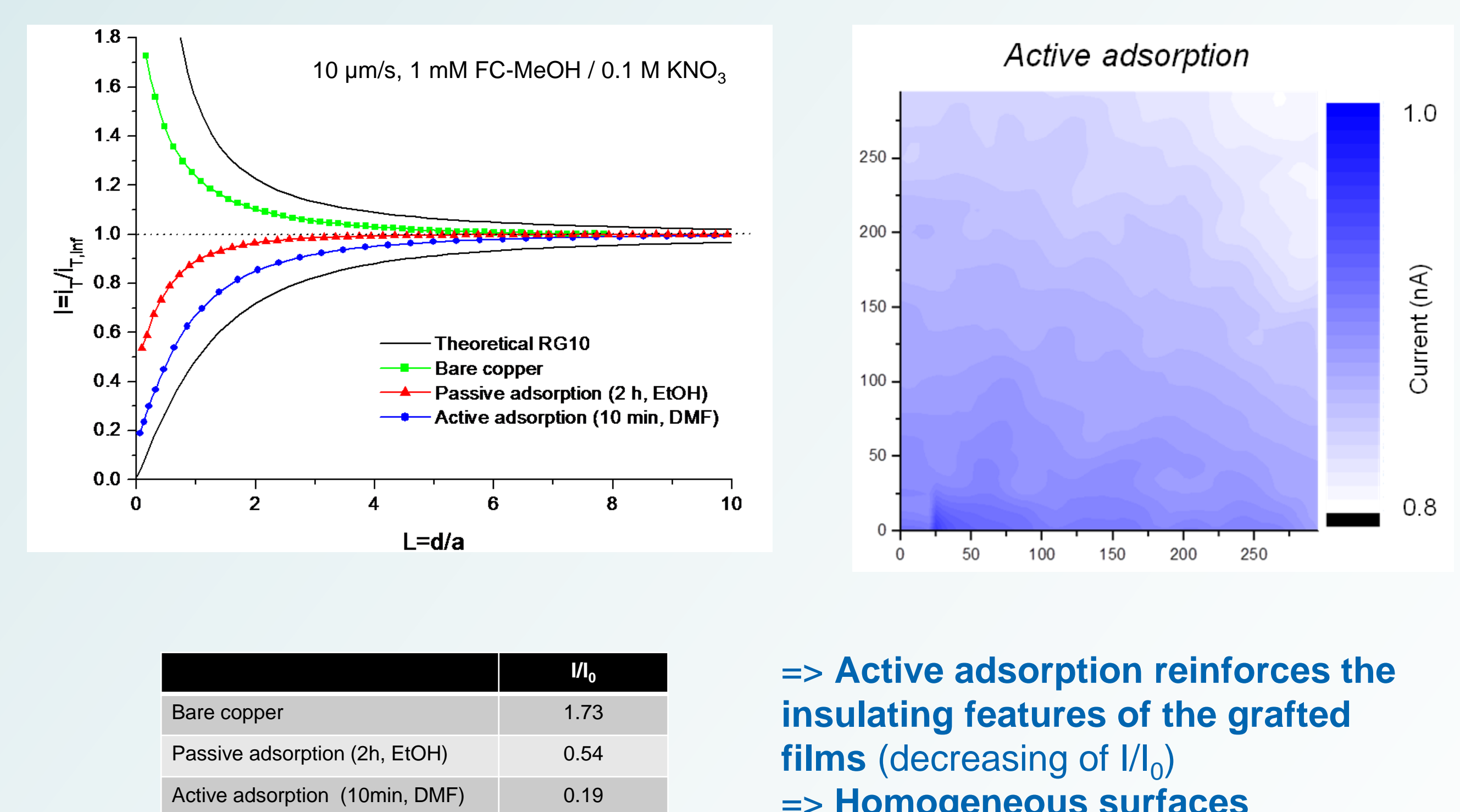
Electrochemical stability (CV, cath. desorption)



Protection against corrosion (pol. curves)



Local characterization: SECM



Conclusions and perspectives

- Efficiency of active electro-assisted adsorption of organothiols on copper** => formation of SAMs with **excellent properties of organization, protective against corrosion, with high electrochemical stability**, and formed with a **significant saving of time** comparatively to the *passive* methodology (10min vs. 2h).
- Perspectives: variation and optimization of experimental conditions with other substrates and surfactants [3], use of ionic liquids (to reduce hydrocarbon contaminations), ...

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